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COMPLETE SPECIFICATION

Production of Acrylates and Methacrylates

We, ROHM & HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 222 West Washington Square, Philadelphia 5, Pennsylvania, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with a method for producing esters of acrylic and methacrylic acid by transesterification.

In accordance with the present invention, there is provided a method for the preparation of an ester of acrylic or methacrylic acid by transesterification which comprises (A) heating a mixture containing (1) a primary or secondary alcohol reactor, (2) an ester reactant which is an ester of acrylic or methacrylic acid with an alcohol and which is lower boiling than the desired ester product, (3) at least one phenate of sodium, potassium or lithium as catalyst and, if necessary, (4) a polymerization inhibitor other than the phenate catalyst and (B) distilling off an azeotrope of the ester reactant and the alcohol liberated by the transesterification reaction.

In carrying out the above method, the amount of phenate catalyst in the reaction mixture is maintained in the range from 0.2 to 8 mole per cent of the alcohol reactant and the alkali metal content of the reaction mixture is, throughout the transesterification reaction, maintained at no more than stoichiometric with respect to that amount of free phenol which corresponds to the amount of phenate present. Preferably, the reaction mixture contains some free phenol corresponding to the phenate catalyst employed.

The simplest catalyst used in the method

of the invention is an unsubstituted phenate but catalytically effective ring-substituted phenates, i.e. phenates carrying one or more substituents which do not materially detract from the catalytic property of the parent unsubstituted phenate, may also be used. Examples of substituted phenate catalysts are mono- and di-substituted phenates in which the substituents (e) is or are C₁—C₂ alkyl, C₁—C₂ alkoxy, amino, C₁—C₂ alkylamino, phenylamino or phenyl. These latter substituents are preferably situated in the meta and/or para positions.

The preferred catalyst is either an unsubstituted phenate or a mono-substituted phenate in which the substituent, which is preferably in the meta or para position, is one of the groups listed above. Preferred ester reactants are lower, i.e. C₁—C₂ alkyl acrylates or methacrylates, particularly the methyl esters.

Experiments conducted with the preferred type of catalyst set forth in the preceding paragraph have shown the method of the invention to be applicable to a wide range of alcohol reactants without the low yields and lack of reproducibility frequently associated with prior art methods of transesterification of acrylic esters, particularly acrylates, using basic media. Such low yields have resulted from competing side reactions, such as anionic polymerization and addition of alcohol reactant to the double bond of the ester reactant. The method of the invention is of particular utility when the alcohol reactant is an alcohol other than dimethylaminoethanol. This is so, because the improvements generally obtainable by the method of the invention are less marked when this particular amino compound is used as the alcohol reactant.

As indicated above, it is preferred to use

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methyl or ethyl acrylate or methacrylate as the ester reactant. Propyl and butyl esters may be employed but with no particular advantage. Quite generally, however, the only

5 real restriction on the acrylate or methacrylate reactant is that it be lower boiling than the contemplated product.

The alcohol employed in the present process must contain a greater number of carbon

10 atoms than the alcohol moiety of the acrylate or methacrylate reactant, previously discussed. Suitable alcohols include monohydric and

15 polyhydric types and the alcohol groups need to be primary or secondary in nature in order to participate in the present reaction. Tertiary alcohol groups may be present in the

20 alcohol reactant but such tertiary groups will not actively participate in the reaction. Suitable alcohols include alkanols of 2 to

25 18 carbon atoms; alkoxyalkanols in which the alkoxy group contains from 1 to 18 carbon atoms and the alkanol residue contains 2 to 6 carbon atoms; alkenoxyalkanols in which

30 the alkenoxy group contains 2 to 18 carbon atoms and the alkanol residue contains 2 to 6 carbon atoms; alkenols of 3 to 18 carbon atoms; phenoxyalkanols in which the alkanol

35 residue contains 2 to 6 carbon atoms or such phenoxyalkanols which contain one or more alkyl ring substituents contributing a total

40 of not more than 18 carbon atoms; phenoxy-alkoxyalkanols, or phenoxyalkoxyalkanols containing up to 50 alkoxy residues, in which

45 the alkanol residue contains 2 to 6 carbon atoms and in which each alkoxy residue is an ethoxy or propoxy residue; phenoxyalkoxy-alkanols and phenoxyalkoxyalkanols as

50 just defined but which contain one or more alkyl ring substituents contributing a total of not more than 18 carbon atoms; cycloalkanols

55 of 4 to 8 carbon atoms or such cycloalkanols containing one or more alkyl ring substituents contributing a total of not more than 18 carbon atoms; phenylalkanols in which the

60 alkanol residue contains 1 to 12 carbon atoms or such phenylalkanols containing one or more alkyl ring substituents contributing a total of not more than 12 carbon atoms; dialkyl-

65 aminocycloalkanols in which the alkanol residue contains 2 to 6 carbon atoms and the two alkyl groups contain a total of 2 to 16 carbon atoms; *tert*-alkylaminoalkanols in which the

alkanol residue contains 2 to 6 carbon atoms and the tertiary alkyl group contains 4 to 18 carbon atoms; glycols and glycerols of

2 to 18 carbon atoms in which the hydroxyl groups are on different carbon atoms; and other polyhydric alcohols of up to 18 carbon

atoms in which the hydroxyl groups are on different carbon atoms.

Typical of the alcohols that may be employed are ethanol, butanol, hexanol, decanol, dodecanol, hexadecanol, and octa-

decanol, methoxydecanol, methoxyhexadecanol, ethoxy-

ethanol, ethoxyoctanol, ethoxydodecanol, propoxypropanol, propoxyheptanol, propoxyundecanol, butoxybutanol, butoxytetradecanol,

70 hexoxyhexanol, hexoxydodecanol, octoxynonanol, octoxydecanol, nonoxynonanol, decoxybutanol, dodecoxyhexanol, benzyl alcohol, phenylethanol, phenylbutanol, phenyl-

75 decanol, phenyldodecanol, methylphenylmethanol, butylphenyloctanol, dibutylphenylethanol, octylphenylethanol, nonylphenylpropanol, cyclohexanol, butylcyclohexanol, octyl-

cyclohexanol, propylcycloheptanol, phenoxytriethoxyethanol, phenoxytripropoxypropanol, butylphenoxyethoxyethanol, octylphenoxy-

80 ethoxyethanol, ethylene glycol, diethylene glycol, hexamethylene glycol, decamethylene glycol, octadecamethylene glycol, phenoxyethanol, phenoxybutanol, butylphenoxy-

85 pentanol, octylphenoxyethanol, ethylphenoxyhexanol, propenol, hexenol, octenol, decenol, dodecenol, octadecenol, vinoxethanol, vinox-

90 hexanol, propenoxypentanol, butenoxypentanol, butenoxypentanol, octenoxypentanol, dodecenoxypentanol, octadecenoxypentanol, propynol, butynol, hexynol, dodecynol, dimethylamino-

95 ethanol, diethylaminoethanol, dibutylaminoethanol, diethylaminobutanol, *tert*-butylaminobutanol, *tert*-octylaminobutanol, *tert*-dodecylaminobutanol, *tert*-octyldodecylamino-

ethanol, and glycerol pentaerythritol.

If the phenate catalyst itself serves as a satisfactory polymerization inhibitor, no additional inhibitor is required. Otherwise, there

100 may be employed, in the usual amounts, an inhibitor such as hydroquinone, diphenylphenylene diamine, and *p*-hydroxydiphenylamine, the latter compound, in the form of

an alkali metal phenate, also being useful as a catalyst.

The phenate catalyst may be prepared by reacting an appropriate phenol with an

105 alkoxide of sodium, potassium or lithium. If the alcohol liberated by this reaction is present in the reaction mixture subjected to transesterification, it will obviously be desirable that such alcohol either be the same

110 as the alcohol reactant or the same as the alcohol from which the ester reactant is derived. Otherwise, unnecessary mixtures of alcohols will be present in the reaction

115 mixture.

The phenate catalyst may be formed *in situ* from the phenol and the alkali metal alcoholate or it may be preformed from the

120 phenol and alkali metal alcoholate and the resulting mixture introduced in to the reaction mixture to be subjected to transesterification. In either case, however, the phenol

125 should be employed in an amount which is at least stoichiometric with respect to the alcoholate. In this way, the alkali metal content of the reaction mixture undergoing transesterification is no more than stoichiometric

130 with respect to that amount of free phenol

which corresponds to the amount of phenate present.

If it is desired to prepare the phenate catalyst *in situ*, the preferred procedure is to introduce initially the phenol, in an amount which is at least stoichiometric, and which is preferably more than stoichiometric, with respect to the alcoholate which is to be added during the reaction period. This is perhaps the simplest and most preferred method. It is merely necessary to select in advance the amount of phenate catalyst to be used and then ensure that the phenol is initially introduced in at least equimolar amounts with respect to the alcoholate added later.

For forming the phenate catalyst, commercially available alcoholic, usually methanolic, solutions of alkali metal alcoholate are quite satisfactory. Typical, in this respect, is a methanolic 25% solution of sodium methoxide.

It is, also, possible to prepare and isolate the phenate catalyst before use. It may then be added in any convenient manner, such as suspended in the ester reactant, as desired.

In the present reaction, it is preferred to employ the ester reactant in amounts of 1.2 to 3.0 moles, or more, per hydroxyl group in the alcohol reactant. With such a range of proportions, separation of the desired product is greatly facilitated.

It is required under the present invention to employ 0.2 to 8 mole per cent of the phenate to the alcohol reactant, preferably 0.5 to 5 mole per cent. The catalyst is preferably added, or formed *in situ*, either continuously or portionwise during the course of reaction. When the provision of catalyst is effected portionwise, increments of catalysts are best provided at frequent intervals.

It is preferable to conduct the present reaction in the substantial absence of water since water reacts with the phenate and thereby impairs the efficiency of the reaction. However, if the presence of water is contemplated, then there must be added sufficient additional phenate to accommodate the anticipated water. It can be readily seen that it is advantageous to conduct the reaction with a minimum amount of water present.

The present reaction will, in general be carried out at a temperature in the range 60° to 150° C., preferably 70° to 110° C., the actual temperature, of course, depending upon the azeotropic distillation temperature of the ester reactant and the liberated alcohol. Reduced pressures may be used in order to avoid excessively high pot temperatures during the removal of the azeotropic distillate.

The method of the invention will be more fully understood from the following examples which are offered by way of illustration and not by way of limitation. In the examples, parts are by weight unless otherwise indicated, and in all cases the phenate catalyst

and alkali metal contents of the reaction mixture are maintained within the ranges heretofore indicated as essential.

EXAMPLE 1

To a flask equipped with stirrer, thermometer, addition funnel and fractional distillation column are charged the following materials—270 parts of 1,3-butanediol, 1200 parts of methyl methacrylate, and 6 parts of *p*-hydroxydiphenylamine.

The pressure is reduced to 400 mm. and the charge is heated to 70° C. At this temperature, the initial addition of catalyst is made. The catalyst solution consists of 6.4 parts of methanolic 25% sodium methoxide and 5.6 parts of *p*-hydroxydiphenylamine, diluted with methanol to a total volume of 15 ml. to keep the resulting sodium derivative of the *p*-hydroxydiphenylamine completely in solution. Reflux of the methanolmethyl methacrylate azeotrope begins in the still head and, as soon as the heat temperature decreases to 49° C., takeoff is started. At this time, a further addition of catalyst is started and is continued throughout the reaction period. This catalyst solution is made up by combining 5.8 parts of methanolic 25% sodium methoxide with 5.0 parts of *p*-hydroxydiphenylamine with further dilution with methanol to a total volume of 18 ml. During the reaction period, this solution is added in 0.5 ml. portions at 5-minute intervals from the dropping funnel.

Removal of azeotropic distillate at a head temperature of 49° to 50° C. under a pressure of 400 mm. is completed in 3.5 hours, at which time the head temperature can no longer be held below 50° C., even at total reflux. Estimation of the methanol content of the azeotropic distillate by means of refractive index measurement shows that the transesterification has reached completion. The pressure in the system is then lowered gradually and unreacted methyl methacrylate is recovered by distillation until distillate ceases coming over with a pot temperature of 85° C. at a pressure of 3 mm. absolute pressure.

The stripped, crude ester is then distilled through a short column. After a small fore-run of 5 parts, the product, 1,3-butanediol dimethacrylate, is taken overhead at 77.5° to 79° C. at 0.4 mm. absolute pressure. The product weighs 613 parts; 90.4% yield, based on the glycol.

Analyses: Saponification No. 493
(Calculated—496)

Acid No. 0.0

n_D^{20} —1.4523

A duplicate experiment, with amounts and conditions as described above, gives a 91.6% yield with a transesterification time of 3.1 hours.

Similar results are obtained by employing

potassium ethoxide in place of sodium methoxide and *p*-phenylphenol in place of *p*-hydroxydiphenylamine.

In like manner, there are made methylcyclohexyl acrylate from ethyl acrylate and methylcyclohexanol; phenylethyl methacrylate from phenylethanol and methyl methacrylate; and octadecyl methacrylate from ethyl methacrylate and octadecanol.

For comparison, a series of experiments is carried out under similar operating conditions but with omission of the phenolic compound or with its use in less than a 1:1 mole ratio with the sodium methoxide. Results are erratic, with ester yields varying down to about 40%. Relatively large polymeric residues are obtained.

EXAMPLE 2

The following materials are charged to a flask equipped with a stirrer, thermometer, addition funnel and fractional distillation column—270 parts 1,3-butanediol, 900 parts methyl methacrylate, and 4.5 parts hydroquinone.

A catalyst mixture is prepared by suspending 14.0 parts of powdered sodium phenoxide in sufficient methyl methacrylate to give a total volume of 48 ml.; a slow stream of nitrogen is used to keep the solid uniformly suspended during use.

The system pressure is decreased to 300 mm. absolute pressure and heat is supplied. When the batch temperature reaches 70° C., an initial addition of 12 ml. of the catalyst suspension is made. Thereafter, at five-minute intervals, 1 ml. portions of the catalyst suspension are added during the reaction period.

Over a period of three hours, an azeotropic distillate of methanol and methyl methacrylate is removed at a vapor temperature of 43° to 48° C. A total of 367 parts of distillate is obtained, whose methanol content is 51.6%. The vapor temperature can no longer be maintained below 48° C., indicating no further production of methanol by the transesterification reaction. The pressure is then gradually reduced and unreacted methyl methacrylate is removed by distillation. The residual reaction mixture is cooled, filtered to remove solids and washed with aqueous 20% sodium hydroxide solution. The organic layer is stripped under a pressure of 0.5 mm. absolute pressure to a final pot temperature of 50° C. The residual product is stirred for 1 hour at 50° C. with activated carbon and filtered to obtain 580 parts (85.5% yield) of 1,3-butanediol dimethacrylate. It is pale amber in color and has a refractive index, n_D^{20} 1.4526; saponification No. 489 (calculated 496); acid No. 0.0.

Using similar reaction conditions, triethylene glycol is substituted for 1,3-butanediol to obtain a 79% yield of the dimeth-

acrylate of triethylene glycol, n_D^{20} 1.4602; saponification No. 384 (calculated 392).

EXAMPLE 3

To a transesterification system are added—270 parts 1,3-butanediol, 1200 parts methyl methacrylate, and 24 parts *p*-hydroxydiphenylamine.

A sodium methoxide solution is prepared by diluting 26 parts of methanolic 25% sodium methoxide with additional methanol to a total volume of 48 ml.

The pressure in the system is reduced to 400 mm. absolute pressure, an initial addition of 12 ml. of the sodium methoxide solution is made and the batch is heated to reflux. Takeoff of methanol-methyl methacrylate distillate through an efficient fractional distillation column begins when the pot temperature reaches 79° C., with a vapor temperature of about 54° C. Over a period of three hours, additional sodium methoxide solution is introduced continuously at a rate of 12 ml. per hour. The reaction is complete in three and one-half hours, as indicated by rising vapor temperature when no more methanol is produced by the transesterification reaction. The pot temperature at this time rises to 102° C.

The pressure is gradually reduced while distilling out unreacted methyl methacrylate. The product, 1,3-butanediol dimethacrylate, is then taken overhead at a vapor temperature of 81° to 87° C. under a pressure of 0.5 mm. absolute pressure. It weighs 612 parts, corresponding to a yield of 90%, based on 1,3-butanediol.

In a like manner, a molar equivalent amount of phenol is substituted for the *p*-hydroxydiphenylamine used in this example for *in situ* generation of the sodium phenate transesterification catalyst. Preferably, if phenol is used, a small amount of a free radical polymerization inhibitor, such as diphenylphenylene diamine or hydroquinone, should also be added since phenol itself is not an adequate inhibitor to guard against free radical polymerization during the heating period. Likewise, instead of *p*-hydroxydiphenylamine or phenol, *p*-methoxyphenol is used for *in situ* generation of the transesterification catalyst; it serves also as a good polymerization inhibitor so that no other inhibiting material need be added.

Similarly, glycerol trimethacrylate is prepared from methyl methacrylate and glycerol reacted in the presence of sodium dimethylaminophenate.

EXAMPLE 4

Using equipment as described in previous examples, the following materials are charged initially—390 parts 2-ethylhexanol, 750 parts ethyl acrylate, and 4 parts diphenylphenylene diamine. A catalyst mixture is made up by

combining 28 parts of sodium phenoxide with 75 ml. of ethyl acrylate (96 ml. total volume). The phenoxide is kept in suspension by means of a slow stream of nitrogen.

- 5 Heat is supplied to the flask and, when the temperature of the charge reaches 90° C., an initial addition of 12 ml. catalyst suspension is added from the dropping funnel. Reflux of ethyl acrylate-ethanol azeotrope
10 begins within three minutes and takeoff of distillate is begun, the rate of takeoff being adjusted so that the head temperature remains between 77.5° and 82° C. During the reaction period, 2 ml. portions of catalyst suspension are added at 5-minute intervals. Heating and distillation of the azeotrope are continued for 3.3 hours.

- The reaction mixture is then strip distilled to remove unreacted ethyl acrylate and to
20 obtain 546 parts of a crude ester distillate. This distillate is washed with aqueous 20% sodium hydroxide and is then redistilled with fractionation to obtain, after removal of a lower-boiling forerun, 386 parts of 2-ethylhexyl acrylate, boiling at 50° C. at about
25 1 mm. It has a saponification No. of 305 (calculated 305); n_D^{20} 1.4352.

- In a like manner, by substituting benzyl alcohol for the 2-ethylhexyl alcohol used
30 above, benzyl acrylate is obtained in good yield. Similarly, there is prepared octylphenoxyethyl acrylate from octyl acrylate and octylphenoxyethanol reacted in the presence of potassium aminophenolate or lithium dodecylphenolate.

- 35 Under similar reaction conditions but with equivalent amounts of sodium methoxide substituted for the sodium phenoxide used above, two attempted reactions give 2-ethylhexyl acrylate yields of 11 and 28% in the main distillation fractions. Very large non-distillable
40 residues are obtained in these distillations.

EXAMPLE 5

- A sodium methoxide solution is prepared by
45 dissolving 0.16 part of sodium metal in 21 ml. of methanol. To a flask equipped with stirrer, thermometer, addition funnel and a fractional distillation column are charged —600 parts methyl methacrylate, 4 parts *p*-hydroxydiphenylamine, 176 parts 2-vinoyethanol, and 3 ml. sodium methoxide solution. The mixture is heated to reflux and
50 addition of the remainder of the sodium methoxide solution is begun in 0.5 ml. portions at 5-minute intervals and is continued during the reaction period until all has been introduced. Over a period of three hours,
55 140 parts of a binary, azeotropic distillate of methanol and methyl methacrylate is removed with the takeoff rate so adjusted that the vapor temperature remains at about 70° C. until within the last few minutes of the reaction period when the temperature is allowed to rise to about 99° C.

The reaction mixture is cooled, 2 parts of *p*-hydroxydiphenylamine is added and unreacted methyl methacrylate is then removed by distillation under gradually reduced pressure. After removal of a small (5 parts) intermediate fraction, 283 parts of 2-vinoyethyl methacrylate is obtained, boiling point 63° C. at 4.5 mm. absolute pressure; n_D^{20} 1.4479; saponification No. 359 (calculated 360); acid No. 0.0.

In like manner, there are prepared methoxybutyl methacrylate from ethyl methacrylate and methoxybutanol; octenyl acrylate from propyl acrylate and octenol; and phenoxyethyl methacrylate from butyl methacrylate and phenoxyethanol.

EXAMPLE 6

To a flask equipped with stirrer, thermometer, addition funnel and fractional distillation column are charged the following materials: 500 parts 2,2-dimethyl-3-dimethylaminopropanol, 800 parts methyl methacrylate, and 40 parts *p*-hydroxydiphenylamine. A sodium methoxide solution is prepared by diluting 41 parts of methanolic 25% sodium methoxide with additional methanol to a total volume of 60 ml. The contents of the flask are heated to 90° C. and 12 ml. of the sodium methoxide is added. Thereafter, additional small portions of the sodium methoxide solution are introduced at frequent intervals over a 4-hour period at an average usage of 12 ml per hour. Methanol formed by the transesterification reaction (plus that introduced in the sodium methoxide solution) is removed by distillation as a binary azeotrope with methyl methacrylate. The takeoff rate is adjusted to maintain a vapor temperature in the range of 68° to 72° C. The transesterification reaction is complete in five hours. Excess, unreacted methyl methacrylate is then removed by distillation under reduced pressure. Distillation is continued to obtain 610 parts of 2,2-dimethyl-3-dimethylaminopropyl methacrylate, boiling point 69° to 72° C. at 2 mm. absolute pressure; n_D^{20} 1.4417; nitrogen content 7.0% (calculated 7.0%); purity by bromine absorption 98.4%.

In a similar manner, by substituting 2-dimethylaminoethanol for the 2,2-dimethyl-3-dimethylaminopropanol used above, high yields of 2-dimethylaminoethyl methacrylate are obtained. Likewise, from 2-dimethylamino-2-methylpropanol there is obtained 2-dimethylamino-2-methylpropyl methacrylate.

Similarly, there are prepared cyclohexyl methacrylate from cyclohexanol and methyl methacrylate; octylphenoxyethoxyethyl acrylate from methyl acrylate and octylphenoxyethoxyethanol, containing ten ethoxy units; and *tert*-octylaminoethyl methacrylate from *tert*-octylaminoethanol and butyl methacrylate.

WHAT WE CLAIM IS:—

1. A method for the preparation of an ester of acrylic or methacrylic acid by transesterification which comprises (A) heating a mixture containing (1) a primary or secondary alcohol reactant, (2) an ester reactant which is an ester of acrylic or methacrylic acid with an alcohol and which is lower boiling than the desired ester product, (3) at least one phenate of sodium, potassium or lithium as catalyst and, if necessary, (4) a polymerization inhibitor other than the phenate catalyst and (B) distilling off an azeotrope of the ester reactant and the alcohol liberated by the transesterification reaction, wherein the amount of phenate catalyst present in the reaction mixture is from 0.2 to 8 mole per cent of the alcohol reactant and the alkali metal content of the reaction mixture throughout the transesterification reaction is no more than stoichiometric with respect to that amount of free phenol which corresponds to the amount of phenate present.
2. A method according to Claim 1, wherein the reaction mixture contains free phenol corresponding to the phenate catalyst.
3. A method according to Claim 1 or 2, wherein the alcohol reactant is an alcohol other than dimethylaminoethanol.
4. A method according to Claim 1, wherein the phenate catalyst is sodium, potassium or lithium phenoxide.
5. A method according to Claim 1, wherein the phenate catalyst is a mono-substituted phenate in which the substituent is a C_1-C_{12} alkyl, C_1-C_{12} alkoxy, amino, C_1-C_4 alkyl-amino, phenylamino or phenyl group.
6. A method according to Claim 4 or 5 in which the transesterification reaction is carried out at a temperature of 60° to 150° C.
7. A method according to Claim 6 in which the transesterification reaction is carried out at a temperature from 70° to 110° .
8. A method according to any one of Claims 4-7, wherein the phenate catalyst is present in an amount of from 0.5 to 5 mole per cent of the alcohol reactant.
9. A method according to any one of Claims 4-8, wherein the reaction mixture contains free phenol corresponding to the phenate catalyst.
10. A method according to any one of Claims 4-9, wherein the ester reactant is a C_1-C_4 alkyl acrylate or methacrylate.
11. A method according to Claim 10, wherein the ester reactant is methyl acrylate or methyl methacrylate.
12. A method according to any one of Claims 4-11, wherein the alcohol reactant is a C_2-C_{18} alkanol; an alkoxyalkanol in which the alkoxy group contains from 1 to 18 carbon atoms and the alkanol residue contains from 2 to 6 carbon atoms; an alkenoxyalkanol in which the alkenoxy group contains from 2 to 18 carbon atoms and the alkanol residue contains from 2 to 6 carbon atoms; a C_3-C_{18} alkenol; a phenoxyalkanol in which the alkanol residue contains from 2 to 6 carbon atoms or such phenoxyalkanol which contains one or more alkyl ring substituents contributing a total of not more than 18 carbon atoms, a phenoxyalkoxyalkanol, or phenoxyalkoxyalkoxyalkanol containing up to 50 alkoxy residues in each of which the alkanol residue contains from 2 to 6 carbon atoms, in each of which each alkoxy residue is an ethoxy or propoxy residue; a phenoxyalkoxyalkanol or phenoxyalkoxyalkoxyalkanol as defined above and which contains one or more alkyl ring substituents contributing a total of not more than 18 carbon atoms; a C_2-C_6 cycloalkanol or such cycloalkanol containing one or more alkyl ring substituents contributing a total of not more than 18 carbon atoms; a phenyl-alkanol in which the alkanol residue contains from 1 to 12 carbon atoms or such phenyl-alkanol containing one or more alkyl ring substituents contributing a total of not more than 18 carbon atoms; a C_3-C_{18} alkyne; a *tert*-alkylaminoalkanol in which the alkanol residue contains from 2 to 6 carbon atoms and the tertiary alkyl group contains from 4 to 18 carbon atoms; or a C_2-C_{18} polyhydric alcohol in which the hydroxyl groups are on different carbon atoms.
13. A method according to any one of Claims 4-11, wherein the alcohol reactant is a dialkylaminoalkanol in which the alkanol residue contains from 2 to 6 carbon atoms and the two alkyl groups contain between them a total of from 2 to 16 carbon atoms.
14. A method according to any one of Claims 4-13, wherein the phenate catalyst is formed *in situ*.
15. A method according to any one of Claims 4-13, wherein the phenate catalyst is added to the reaction mixture, or formed *in situ* therein, continuously or portionwise during the course of the reaction.
16. A method according to Claim 4, when carried out substantially as hereinbefore described with reference to any one of the foregoing Examples.
17. An ester of acrylic or methacrylic acid whenever prepared by a method according to any one of Claims 1-3.
18. An ester of acrylic or methacrylic acid whenever prepared by a method according to any one of Claims 4-16.

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